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Rotational spectrum of three conformers of 3,3-difluoropentane: Construction of a 480 MHz bandwidth chirped-pulse Fourier-transform microwave spectrometer

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ABSTRACT

The rotational spectra for three conformers of 3,3-difluoropentane have been measured using both a newly constructed narrow bandwidth chirped-pulse Fourier-transform microwave spectrometer and a Balle–Flygare resonant cavity Fourier-transform microwave spectrometer. The chirped-pulse instrument produces a microwave pulse spanning up to 480 MHz bandwidth in the 7–18 GHz region by mixing a 1 μs chirped pulse (of up to 240 MHz bandwidth) from an arbitrary function generator with the output from a microwave synthesizer.

Rotational spectra for the normal isotopic species and all possible ^{13}C single substitutions were observed for the gauche–gauche and anti-gauche conformers, allowing a Kraitchman substitution structure and an inertial fit structure to be determined. ^{13}C isotopic species and dipole moment components were not measurable for the less intense anti–anti species as a result of partially resolved fine splitting. Details of the new chirped-pulse instrument will be described and the structural results will be presented and compared with ab initio data for 3,3-difluoropentane.

1. Introduction

The recent introduction of broadband chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometers by Pate [1,2] and Cooke [3] has provided a powerful new tool for the assignment of complex microwave spectra. However, the cost of chirped-pulse instruments that are capable of recording a full 11 GHz broadband spectrum with each gas pulse exceed the typical budget of research groups at smaller institutions. Fortunately, the technology is easily adaptable to enable the instrument's bandwidth to be adjusted to fit within the desired price range [3]. We report here on the construction of a scaled-down CP-FTMW spectrometer that has a bandwidth of up to 480 MHz, providing significant advantages over resonant cavity FTMW spectrometers of the Balle–Flygare type [4].

Our incentive to construct such an instrument lies in its potential for the study of exotic species such as ions or radicals, where it increases the probability for location of spectral transitions, a concept already proven by coupling such an instrument with a laser ablation source [3]. CP-FTMW spectrometers thereby provide a practical solution for simplifying the optimization process for source conditions in pulsed discharge nozzle or laser ablation experiments. With good quality ab initio predictions able to provide estimates of rotational constants to within a few percent of experiment, the likelihood of rotational transitions for an unknown species falling within one or two frequency steps of the 480 MHz bandwidth spectrometer is high, thereby greatly reducing the amount of time spent in searching. Even for collection and interpretation of microwave spectra of stable and neutral molecular species, there are clear advantages over a standard Balle–Flygare instrument. For instance, the acquisition of a survey spectrum spanning the full 7–18 GHz region (even a spectrum having a relatively poor signal to noise ratio) offers improved confidence in spectral assignment since it is much more likely that significant spectral features (such as the existence of vibrationally excited states or tunneling or inversion motions) will be promptly identified.

We report in this paper on the initial construction and testing of a 480 MHz bandwidth instrument, focusing on the assignment of the rotational spectra of three conformers of the straight chain alkane, 3,3-difluoropentane. This molecule, with total dipole moments of all three conformers predicted in the range 2.5–2.8 D, provides a perfect candidate for testing and optimization of this new system and illustrates the usefulness of a scaled-down broadband microwave spectrometer, at a cost which makes it more affordable for principally undergraduate institutions.

The 3,3-difluoropentane has four conformers (arising from rotation about the two C–C single bonds connected to the central

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carbon atom – see Fig. 1). In a recent FT-microwave study of pentane [5], only spectra for anti–anti (aa) and anti-gauche (ag) species were assigned, while the gauche–gauche (gg) conformer (with methyl groups on opposite sides of the C–C–C plane) and a sterically crowded gauche–gauche′ (gg′) conformer (with methyl groups on the same side of the C–C–C plane) were not observed. This is consistent with the expected order of stability in pentane (where a room temperature distribution of 51% aa, 36% ag, 13% gg is predicted) [5]. Our own recent ongoing studies of a series of straight chain alkanes with Si or Ge substitutions (such as diethylsilane [6,7], diethyldifluorosilane [6], diethylgermane [8], *n*-butylsilane [9] and *n*-butylgermane [10]) also makes 3,3-difluoropentane an interesting addition to this series so that structural comparisons and insights should eventually be possible.

2. Experimental

Design of the narrow bandwidth CP-FTMW instrument used in this study followed basic concepts introduced by Pate [1] for an 11 GHz bandwidth instrument, and later modifications for a reduced (ca. 4 GHz) bandwidth instrument introduced by Cooke [3]. Fig. 2 shows a schematic of our instrument, along with a list of key components. A basic outline of the instrument's operation is given below.

Briefly, a 1 μs duration chirped frequency pulse from an arbitrary function generator ((component (**1**), Fig. 2), Tektronix AFG3251) is mixed (**4**) with the output of an HP8673G microwave synthesizer (**2**) and then amplified via a 10 W solid state microwave amplifier (**5**) (Microwave Power, L0618-40-T646), giving a pulse of up to 480 MHz bandwidth centered around the microwave synthesizer frequency. This polarizing radiation then enters the chamber and is broadcast onto the pulsed molecular gas expansion via a wide-band microwave horn antenna ((**6**), ATM WRD750-442-C3). A Kapton® window (ATM WRD750-230-G3-G3) ensures that vacuum integrity is maintained between the waveguide feedthrough and microwave horn. The gas sample is pulsed through a Parker Hannifin (General Valve) Series 9 nozzle of 0.8 mm diameter orifice (**7**), which is aligned perpendicular to the microwave horns and pulses straight into the throat of a 10 in. Varian VHS-250 diffusion pump.

The vacuum chamber (**8**), an ISO-250 6-way cross with two 8 in. extensions to accommodate the microwave horn antennae, has a volume of approximately 85 L and maintains an idle pressure of mid-10^{-7} Torr, increasing to mid-10^{-5} Torr when gas is pulsed into the chamber. Pulsing rates of 10 Hz are achievable with this vacuum chamber although typically 4 Hz were used in this experiment for optimal scope performance. Sheets of microwave absorbing foam (Emerson and Cuming Eccosorb HR-25/ML) placed in the vacuum chamber prevent cavity resonances, although with the relatively low power used, such resonances have not been observed to be a problem.

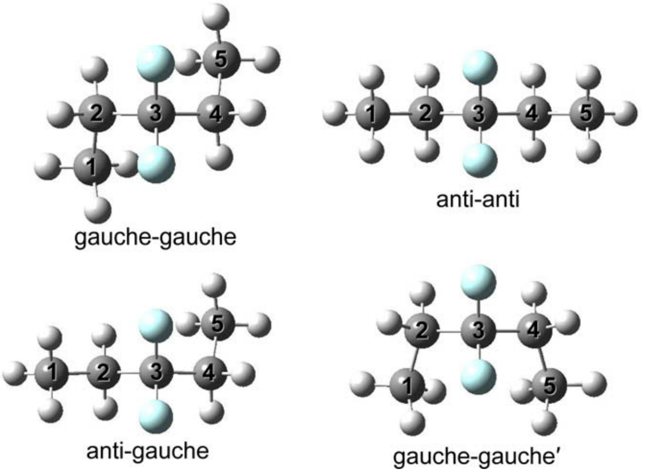

Fig. 1. Structures of the four conformers for 3,3-difluoropentane obtained from ab initio calculations at the MP2/6-311++G(2d,2p) level.

Rotational polarization induced in the molecules by an incoming microwave pulse is detected by a low noise amplifier, LNA ((**10**), Miteq AMF-5F-08001800-14-10P) on the detection side of the circuit; this LNA is protected by an SPST switch ((**9**), HP33102A) during the polarizing radiation pulse. Molecular emission is detected immediately after cessation of the polarizing pulse and the free induction decay (FID) is collected over 20 μs, amplified by the LNA, and then this signal is mixed back down (**4′**) to radiofrequency (RF) with the split output (**3**) from the microwave synthesizer (**2**). This RF signal is finally passed through a 1–500 MHz amplifier ((**11**), Miteq AU-2A-0150) before being sent to an oscilloscope ((**12**), Tektronix TDS 5054B) for averaging and fast Fourier-transformation (FFT). The instrument described here is currently configured such that both upper and lower sidebands are collected simultaneously and absolute frequencies of any transitions are determined by carrying out a second measurement at a slightly offset center frequency; these two files are then compared by a simple peak-picking program written in LabView [11] to determine absolute frequencies of the rotational transitions. More sophisticated peak-picking routines are currently being developed.

Timing for the gas pulse is provided by a Quantum Composers QC9614+ pulse generator that controls an Iota One valve driver, while a second digital delay/pulse generator (Stanford Research Systems DG-535) synchronized to the QC9614+ nozzle pulse provides timing to both the 10 W amplifier (**5**) and LNA protection switch (**9**). All equipment is referenced to a 10 MHz rubidium frequency standard (Stanford Research Systems FS725).

Although the reduced bandwidth instrument described here cannot provide the deep averaging that is possible with the broadband instrument designed by Pate [1,2] (in which multiple nozzles and multiple FID's per gas pulse allow millions of averages to be accumulated over the entire 11 GHz region), spectral intensity in the present study was sufficient to observe spectra for numerous ^{13}C substituted species, which was adequate for initial assignment of multiple conformers.

A sample of 3,3-difluoropentane was prepared by adding 2.15 g (0.025 mol) of a freshly distilled sample of 3-pentanone in 3 mL diglyme to a solution of 0.025 mol of diethylaminosulfur trifluoride in 5 mL of diglyme dropwise at −20 °C under nitrogen. The reaction mixture was warmed to room temperature and stirred for 10 h and was frozen using liquid nitrogen and degassed. The volatile contents were collected in a tube containing 3 mL of $NaHCO_2$ immersed in liquid nitrogen and after warming to room temperature was stirred for 30 min and the volatile material was collected in another tube containing water and stirred for 20 min. Finally the volatile material was collected and purified using trap to trap distillation for a total of three times. The final sample was checked by NMR and IR spectroscopy. To perform the microwave experiment, a small amount of 3,3-difluoropentane vapor was transferred to a 2 L stainless steel tank, pressurized to about 5 atm with He:Ne (17.5%:82.5%, BOC Gases) giving a sample concentration of about 0.4%. This mixture was then delivered to the pulsed nozzle at a constant pressure of about 1.8 bar. Subsequent experiments have proven a sample tank of this concentration to be sufficient to run a 5000 gas pulse sample scan with a 0–240 MHz chirped pulse to provide a spectrum of the entire 7–18 GHz frequency range (amounting to approximately 24 frequency steps). Numerous improvements can almost certainly be made in terms of optimizing the sample and timing conditions and these are currently being explored.